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PART IV]

SECTION A

[Vol. 18

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PART IV]

SECTION A

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**"NOTE ON THE HARMONIC POLARS AND THE  
CAYLEYAN OF A CUBIC"**

*By*

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ABSTRACT

The main object of the present investigation is to reckon with the special geometrical relations, that connect any of the nine harmonic polars of a (bicursal) cubic  $\Gamma$  and its Cayleyan (or Pippian  $\Omega$ ), (which is naturally a curve of the 6th order and 3rd class).  $O$  being any of the nine inflexions of  $\Gamma$ ,  $L$  being the *related* harmonic polar and  $K$  being the point where  $L$  meets the (inflexional) tangent at  $O$ , the following properties represent some of the *novel* results arrived at in this paper:—

(a) that the line-pair  $(M, N)$ , (representing the *degenerate* polar conic of  $K$ ), taken in conjunction with the inflexional tangent  $OK$ , makes up the triad of tangents, that can be drawn from  $O$  to the class cubic— $\Omega$ ;

(b) that  $P, Q$ , being the two points where  $L$  cuts the lines,  $M, N$ , respectively, the six points of intersection of  $L$  with the order sextic  $\Omega$  consist of

(i) the points  $P, Q, K$  (each counted *singly*)  
and (ii) a certain cusp (on  $L$ ), (counted *thrice*),  
(the cuspidal tangent being no other than the line  $L$  itself);

(c) that the osculating conics of  $\Gamma$  at the three ('cognate') sextactic points, lying on  $L$ , possess a *common* self-conjugate triangle which is in a sense *circumscribed* about the Cayleyan  $\Omega$ ;

and (d) that the common self-conjugate of (c) is no else than the  $\triangle OPQ$ . By the way, it may be remarked that the propositions (a), (b), (c) and (d) have been demonstrated in such a way as to throw a *new* light on a certain result, proved in the first instance in the author's "*Note on Conics of double osculations*" (to be published in the next issue of the '*Journal of the National Academy of Sciences*', Allahabad).

## INTRODUCTION

The main purpose of the present paper is to scrutinise the peculiar geometrical relations, that subsist between any of the nine harmonic polars of a (bicursal) cubic and its Cayleyan. Incidentally certain special tangents of the Cayleyan have been reckoned with, and the *common* self-conjugate triangle of a triad of 'cognate' sextactic conics has been talked about and discussed in such a way as to give prominence to the relation, which it bears to the polar conic of the (associated) point of contact of the Cayleyan and the Hessian of the (original) cubic. For the sake of clearness and easy reference, certain results, established in my "*Note on conics of double osculation of a cubic*" have been re-stated in this paper. The greater part of the results arrived at in this paper is believed to be original.

## SECTION I

*(Certain novel properties of a triad of cognate sextactic conics.)*

*Art.* 1. It is common knowledge that a bicursal cubic has, in general

(i) 9 points of inflexion  $\{I_r\}$ ,

(ii) 9 associated harmonic polars  $\{L_r\}$ .

and (iii) 27 sextactic points, lying, three by three, on the 9 lines  $\{L_r\}$ . For felicity of expression, two or three sextactic points, seated on the *same* harmonic polar, will be said to be 'cognate' to one another, and their attached osculating (*i. e.*, six-pointic) conics will be similarly termed 'cognate'. Naturally, then, a (bicursal) cubic possesses altogether 9 triads of 'cognate' sextactic conics (real or imaginary). The investigation of the peculiar geometrical relations, subsisting amongst

the three sextactic conics of any of the nine 'cognate' triads is the main objective of the present section. For this purpose Cartesian analysis, involving the use of oblique axes, will be resorted to in the succeeding article.

*Art. 2.* Suppose that any one of the points of inflexion  $[I_r]$  of a given bicursal cubic  $\Gamma$  is chosen as the origin  $O$  of Cartesian coordinates, and that the tangent to  $\Gamma$  at  $O$  is chosen as the axis ( $y=0$ ). If, then,  $\alpha$  be one of the three sextactic points (of  $\Gamma$ ), that have  $O$  for their tangential, and the line  $O\alpha$ ,—which is after all one of the tangents from  $O$  to  $\Gamma$ —be taken as the axis ( $x=0$ ), the Cartesian equation to  $\Gamma$  can be readily thrown into the form :

$$S. y = x^3, \quad \dots \quad (I)$$

where  $S \equiv \alpha x^2 + 2hxy + by^2 + 2gx + 2fy + c = 0$ , ( $A \equiv bc - f^2 = 0$ )  $\dots$  (II)

is the osculating (*i.e.*, six-pointic) conic of  $\Gamma$  at  $\alpha$ . It goes without saying that the Cartesian axes, chosen as above, are in general oblique.

If we now re-write (I) in the form :

$$(S + 3\lambda x^2 + 3\lambda^2 xy + \lambda^3 y^2) y = (x + \lambda y)^3, \quad \dots \quad (III)$$

and prescribe the condition that the line

$$x + \lambda y = 0$$

may touch the conic

$$\left. \begin{aligned} & S + 3\lambda x^2 + 3\lambda^2 xy + \lambda^3 y^2 = 0, \\ \text{i.e., } & (a + 3\lambda)x^2 + 2(h + \frac{3}{2}\lambda^2)xy + (b + \lambda^3)y^2 + 2gx + 2fy + c = 0, \end{aligned} \right\} \dots (IV)$$

we gather

(i) that the other two sextactic conics  $S_1, S_2$ , 'cognate' with  $S$  are given by

$$S_1 \equiv (a + 3\lambda_1)x^2 + 2(h + \frac{3}{2}\lambda_1^2)xy + (b + \lambda_1^3)y^2 + 2gx + 2fy + c = 0 \quad \dots (V)$$

$$\text{and } S_2 \equiv (a + 3\lambda_2)x^2 + 2(h + \frac{3}{2}\lambda_2^2)xy + (b + \lambda_2^3)y^2 + 2gx + 2fy + c = 0 \quad \dots (VI)$$

and (ii) that the associated sextactic points  $\beta$  and  $\gamma$ —naturally 'cognate' with  $\alpha$ —are respectively

$$\left( \frac{\lambda_1}{f - \lambda_1 g}, -\frac{1}{f - \lambda_1 g} \right) \text{ and } \left( \frac{\lambda_2}{f - \lambda_2 g}, -\frac{1}{f - \lambda_2 g} \right), \quad \dots \quad (VII)$$

provided that the two parameters  $\lambda_1, \lambda_2$  are the roots of the quadratic in  $\lambda$ , viz.,

$$c\lambda^2 + B\lambda + 2H = 0. \quad \dots \quad (VIII)$$



$$\begin{vmatrix} ax+hy+g, & hx+by+f, & gx+fy+c \\ 3x, & -\frac{2H}{c}y, & 0 \\ 3y, & 3x-\frac{2B}{c}y, & 0 \end{vmatrix} = 0.$$

This determinantal equation being equivalent to

$$(gx+fy+c)(3cx^2-2Bxy+2Hy^2)=0,$$

the logical conclusion is that the Jacobian of the three 'cognate' sextactic conics  $S, S_1, S_2$ , appertaining to the point of inflexion  $O$ , consists of the related harmonic polar  $L$ , viz.,

$$gx+fy+c=0, \quad \dots \quad (1)$$

and the line-pair  $(M, N)$  defined by

$$3cx^2-2Bxy+2Hy^2=0. \quad \dots \quad (2)$$

That the first line viz.,  $L$  should form a part and parcel of the degenerate cubic

$$\mathcal{J}(S, S_1, S_2)$$

could be foreseen from geometrical considerations. It now remains to scrutinise the geometrical features of the other two lines  $M, N$ .

At the very outset we note that the three pairs of tangents, that can be drawn from  $O$  to the three conics  $S, S_1, S_2$ , as defined by (IX) of the foregoing article, are representable by the *single* Cartesian equation:

$$(B+3c\lambda)x^2-2(H-3/2c\lambda^2)xy+c\lambda^3y^2=0, \quad \dots \quad (3)$$

provided that the parameter  $\lambda$  is allowed to assume the values  $0, \lambda_1, \lambda_2$  in succession.

Recognising, then, that the (necessary and sufficient) condition for the two pairs of lines (2) and (3) to be harmonically conjugate is that  $\lambda$  should satisfy the cubic equation:

$$c\lambda^3+B\lambda^2+2H\lambda\equiv 0,$$

so that the admissible values of  $\lambda$  are, by (VIII) of Art. 2,  $0, \lambda_1, \lambda_2$ , we come to conclude that the three pairs of tangents that can be drawn from  $O$  to  $S, S_1, S_2$  respectively, constitute an involutory system, of which the two focal lines are determined by (2). Hence,

bearing in mind that the harmonic polar  $L$  is the common polar (line) of the point  $O$  w.r.t. the three conics  $S, S_1, S_2$ , we readily realise that the line  $L$  must intersect the three conics in (three) pairs of points, forming an involution of which the two foci (or double points)  $P, Q$  are the two points where  $L$  cuts  $M, N$  respectively.

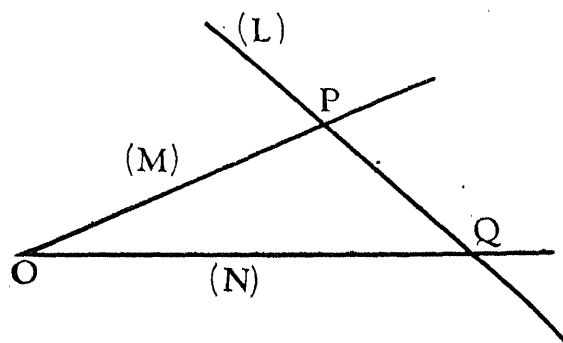


Fig. 2.

Because the polar of  $P$  w. r. t. any of the three conics ( $S, S_1, S_2$ ) goes through both  $O$  and  $Q$ , and the polar of  $Q$  similarly goes through both  $O$  and  $P$  and the polar of  $O$  (viz.,  $L$ ) goes through  $P, Q$ , we are squarely led to the following proposition\* :—

*The cognate sextactic conics ( $S, S_1, S_2$ ), attaching to any of the nine points of inflexion of a bicursal cubic, possess a common self-conjugate triangle whose sides are the three line-constituents of the degenerate Jacobian ( $S, S_1, S_2$ ).*

In Sec. II we shall discuss, among other things, certain novel geometrical properties of the line-pair ( $M, N$ ).

## SECTION II

*(Harmonic polars and other special tangents of the Cayleyan).*

Art. 4. If we now look back upon Art. 2 and adhere to the same notations and conventions, we may, as before, represent a given bicursal cubic  $\Gamma$  in the Cartesian form

$$Sy = x^3 \quad \dots \quad (I)$$

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\*It may be incidentally remarked that the proposition proved above is but a particular phase of a more general proposition, proved by me in my paper on "Conics of double osculation of a cubic." The method, adopted in that paper, is general, whereas the method outlined as above, is rather special, fitting in with the restricted case.

provided that one of the points of inflexion of  $\Gamma$  is taken as the origin  $O$  and the tangent to  $\Gamma$  at  $O$  is taken as the axis ( $y=0$ ) and one of the three tangents (say,  $O\alpha$ ) that can be drawn from  $O$  to  $\Gamma$  is taken as the axis ( $x=0$ ), and the osculating (*i.e.*, six-pointic) conic of  $\Gamma$  at the point of contact  $\alpha$  of this tangent is taken in the form :

$$S \equiv ax^2 + 2hxy + by^2 + 2gx + 2fy + c = 0, \quad (A \equiv bc - f^2 = 0). \quad \dots \quad (II)$$

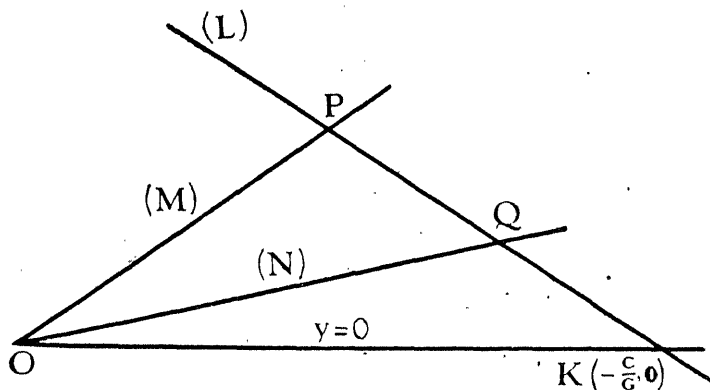


Fig. 3

Harmonic polar ( $gx + fy + c = 0$ )

Since the harmonic polar  $L$  of the inflexion  $O$  is

$$gx + fy + c = 0,$$

the point  $K$ , where  $L$  meets the inflexional tangent ( $y=0$ ), is

$$\left(-\frac{c}{g}, 0\right),$$

and the polar conic of this point *w. r. t.*  $\Gamma$  is easily seen to be

$$3cx^2 - 2Bxy + 2Hy^2 = 0.$$

This being the same as (2) of Art. 3, the inevitable conclusion is that the line-pair  $(M, N)$ , considered in Art. 3, is designable as the (degenerate) polar conic of the point  $K$ . A part of this result could have been anticipated from general considerations. For the polar conic of the inflexion  $O$  being compounded of two lines (*viz.*, the inflexional tangent and the harmonic polar  $L$ ) crossing each other at  $K$ , the polar conic of  $K$  must reciprocally be a pair of lines, crossing each other at  $O$ .



We may now, on the strength of other results proved heretofore, summarise our conclusions in the form of a theorem:—

**THEOREM A.** *The 27 sextactic conics of a bicursal cubic  $\Gamma$  can be distributed into 9 triads of ‘cognate’ conics, attaching respectively to the 9 points of inflexion  $\{I_r\}$ , ( $r=1, 2, \dots \dots 9$ ). Further the three ‘cognate’ (sextactic) conics related to any of the 9 points of inflexion (say,  $I_r$ ), possess a common self-conjugate triangle, whose sides consist of the harmonic polar ( $L_r$ ) of  $I_r$  and the two line-constituents of the (degenerate) polar conic (w. r. t.  $\Gamma$ ) of the point  $K_r$  (on the Hessian), conjugate to  $I_r$ .*

Relying upon the known lemma that the system of polar conics (w. r. t. a given bicursal cubic  $\Gamma$ ) of the  $\infty^1$  points, situated on a given right line (say,  $\Lambda$ ) form a ‘pencil’, whose four common points are the (four) poles of  $\Lambda$ , we promptly perceive, on referring to Fig. 3, that the four poles of the inflexional tangent  $OK$  are the four points of intersection of the two line-pairs :

$$(OK, L) \text{ and } (M, N).$$

Hence the four poles of  $OK$  consist of

$O$  (counted twice),  
and  $P, Q$  (each counted once).

We may accordingly enunciate Theorem A in the following modified form:—

**THEOREM B.** *The 27 sextactic conics of a bicursal cubic  $\Gamma$  can be divided into 9 triads of ‘cognate’ conics, attaching respectively to the 9 points of inflexion  $\{I_r\}$ . Furthermore the three ‘cognate’ (sextactic) conics of the triad related to any particular point of inflexion ( $I_r$ ) admit of a common self-conjugate triangle, whose vertices are the three distinct poles of the (inflexional) tangent to  $\Gamma$  at  $I_r$ .*

**Art. 5.** Referring again to Fig. 3 we notice that  $O, K$  being a pair of ‘conjugate poles’ on the Hessian  $\Gamma'$ , the joining line  $OK$  must be a tangent to the Cayleyan ( $\Omega$ ). Besides, each of the two lines  $M, N$  (i. e.,  $OP, OQ$ ) must be a tangent to  $\Omega$ , seeing that the two lines, taken together, constitute a *degenerate* polar conic of  $\Gamma$  (Art. 4). Thus

$OP$ ,  $OQ$  and  $OK$  must all touch  $\Omega$ . Now  $\Omega$  must be a curve of the third class and sixth degree, for  $\Gamma$  is a *bicursal* cubic. So we have in a way ascertained all the *three* tangents (*viz.*,  $OP$ ,  $OQ$ ,  $OK$ ) that can possibly be drawn from the point  $O$  to the *class-cubic*  $\Gamma$ .

If we now look for the *actual* points of contact (with  $\Omega$ ) of the tangents  $OP$ ,  $OQ$ ,  $OK$  as also  $L$ , we have to bank upon the following well-known lemmas\* of Higher Plane Curves, *viz.*,

(i) that, if  $\gamma$ ,  $\delta$  be a pair of conjugate poles on the Hessian  $\Gamma'$  of a (bicursal) cubic  $\Gamma$ , the four points of contact, (with the Cayleyan  $\Omega$ ) of the two line-pairs, representing the degenerate polar conics of  $\gamma$ ,  $\delta$  will lie on a right line (say,  $\Sigma$ ) ; and

(ii) that the line-pair  $(\Sigma, \gamma\delta)$  constitutes the degenerate polar conic of the *third centre* of the quadrangle, formed by the four poles of the line  $\gamma\delta$  (the other two centres being, of course, the points  $\gamma$ ,  $\delta$  themselves).

What is needed now is to apply the two lemmas (i) and (ii) to the special pair of 'conjugate poles' (on  $\Gamma'$ ), *viz.*,  $O$  and  $K$ .

In the concluding portion of the previous article it has been shewn that the quadrangle, made up of the four poles of the line  $OK$  reduces practically to a triangle *viz.*,  $OPQ$ , so that the three centres of this *degenerate* quadrangle consist of

$O$  (counted twice) and  $K$ .

Consequently, the *third* centre of the quadrangle—as contemplated in lemma (ii)—is none other than the point of inflexion  $O$ , whose (degenerate) polar conic is the line-pair  $(OK, L)$ .

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\*Vide Basset's '*Cubics and Quartics*' (1st edition) Art. 119 (Ch. V),

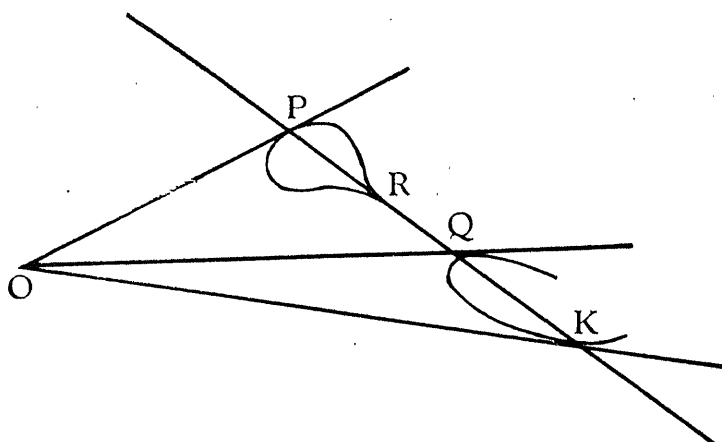


Fig. 4.

Hence the line of collinearity—as guaranteed by lemma (i)—of the four points of contact (with  $\Omega$ ) of the four lines

$$OP, OQ, (OK) \text{ and } L \quad . . . \quad (\text{I})$$

is the right line  $L$ . Palpably, then, the actual points of contact of these lines (with  $\Omega$ ) are respectively

$$P, Q, K \text{ and } R, \quad . . . \quad (\text{II})$$

the last-named point  $R$ , being, of course, a *cusp* (of  $\Omega$ ), the tangent where at is the harmonic polar  $L$ . The adjoining fig. 4 gives a rough idea of the configuration of the several points and lines, that figure in the above discussion.

Apropos of this, it may be remarked that, being an order-sexic  $\Omega$  must cut an arbitrary right line—not excepting  $L$ —at *six* points (real or imaginary). What has been proved heretofore indirectly amounts to saying that *the six points of intersection of the harmonic polar  $L$  with the Cayleyan consist of the cusp  $R$  (counted thrice) and the three simple points  $P, Q$  and  $K$* . It is scarcely necessary to add that similar properties must hold in respect of the hexad of intersections of the Cayleyan  $\Omega$  with each of the remaining eight harmonic polars.

Now according to a well-known lemma, the line  $OK$  touches the Hessian  $\Gamma'$  at the point  $K$ , so that  $\Gamma'$  and  $\Omega$  touch each other at  $K$ , the common tangent thereat being  $OK$ . Inasmuch as each of the three sides of the triangle  $OPQ$  touches  $\Omega$  (the three points of contact being

located on the side  $PQ$ ), we may, in a special sense, speak of  $OPQ$  as a triangle, circumscribed about  $\Omega$ . Hence we are justified in re-stating Theorem A or Theorem B in the following alternative form:—

*Theorem C. The 27 sextactic conics of a bicursal cubic  $\Gamma$  can be arranged into 9 distinct triads, associated respectively with the 9 inflexions of the type  $\{I_n\}$ . Further the three 'cognate' (sextactic) conics, belonging to each of these triads, possess a self-conjugate triangle, circumscribed about the Cayleyan.*

# STUDIES IN THE OPTICAL ROTATION OF ABIETIC ACID.

## Part I Optical rotation in cyclohexane and its derivatives.

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(Received on July 7, 1949.)

The work on the chemistry of rosin dates back to 1826 when Baupé<sup>1</sup> first showed that it contained crystallizable acids. A large amount of work has since been published on the rosin acids and on their relation to the original composition of rosin. Acids of different physical properties have been isolated by different investigators and variously named abietic, pimaric, sylvic, sapinic etc. The empirical formula of these acids were first determined as  $C_{20}H_{30}O_2$  by Trammendorf<sup>2</sup>. Kemner<sup>3</sup> found that the chief constituent of French rosin is pimaric acid whereas the chief constituent of American rosin is abietic acid. Mitra and Ghatak<sup>4</sup> and Rau and Simonsen<sup>5</sup> have established that abietic acid is the chief constituent of Indian rosin from *Pinus longifolia*. The physical properties of abietic acid depend upon the method of preparation and purification but the chemical properties are independent of the same<sup>6</sup>.

Abietic acid was prepared from the best quality Water White rosin from *Pinus longifolia* from Jallo Rosin & Turpentine Factory, Lahore, by distillation in super-heated steam<sup>4</sup>. Great care was taken to use freshly powdered sample of rosin, for powdered rosin on storage gets oxidised.

M. P. 160-63°C

Anal: Calculated for $C_{20}H_{30}O_2$	C—79.47	H—9.93.
Found	C—79.02	H—10.22.

The acid was stored as sodium tetra-abietate and was regenerated as needed from the salt.

Paul Drude<sup>7</sup> gave a general equation for rotatory dispersion

$$[\alpha] = \sum \frac{K}{\lambda^2 - \lambda_0^2}.$$

Each term of the summation has two constants,  $K$  (rotation constant) and  $\lambda_0^2$  (Dispersion constant).

Rotatory dispersion may be classified as "Simple" or "Complex" accordingly as they can or cannot, be expressed by Drude's one term equation

$$[\alpha] = \frac{K}{\lambda^2 - \lambda_0^2}.$$

The abietic acid isolated from Indian rosin was found to obey the simple dispersion formula exactly in solutions in cyclohexane and its derivatives.

Very pure samples of solvents were used in these experiments and the solvents were further purified by distillation. Exact straight lines were obtained (Fig. 1.) when  $1/[\alpha]$  was plotted against  $\lambda^2$ . This is a sufficient proof of the rotatory dispersion being simple. But more stringent numerical tests have been applied and the values are recorded in tables 2 and 3. The difference between the observed rotatory power (o) and that calculated (c) from the dispersion equation are within the limits of experimental error allowed in such measurements.

Generally the deviations lie between  $\pm 0.03^\circ$  but for  $\text{Hg}_{4058}$  a difficult line to read, this difference lies between  $\pm 0.09^\circ$ .

The specific rotatory power of abietic acid for  $\text{Hg}_{4358}$  in different solvents are given in table 1.

The influence of the solvent on the rotation of an optically active substance has been the subject of repeated investigations, Walden<sup>8</sup>

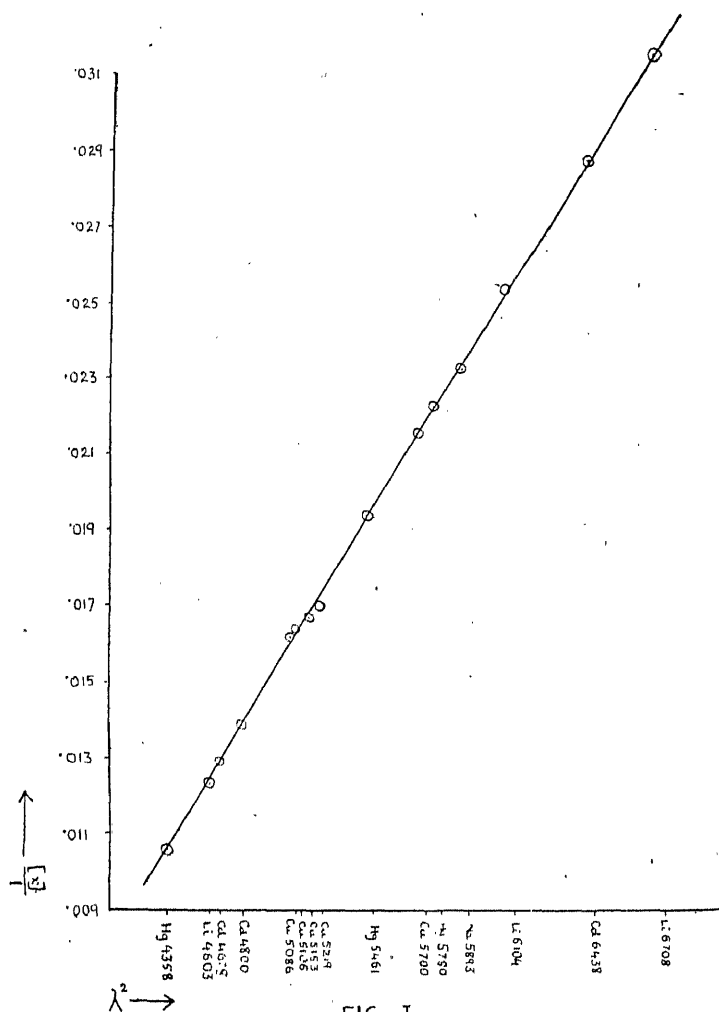


FIG - I

established that there exists a connection between the osmotically determined molecular size and of the active solute and its rotation in the same solvent. The relationship between the degree of association and the rotation is not, however, revealed in a simple parallelism but each constituent of the solution exercises a constitutive influence on the value of rotation. Nernst<sup>9</sup> and Meldrum and Turner<sup>10</sup> showed that the dielectric constant of the solvent was the controlling factor on optical rotation apart from any chemical action.

Table 1

Solvent		Dielectric constant	$\left[ \alpha \right]_{5461}^{25^\circ}$	K	$\lambda_o$ A°U.	Dispersion ratio $\frac{\alpha_{4358}}{\alpha_{5461}}$
1. Cyclohexane ..	...	2.05	—21.46	5.14	2429	1.831
2. Methyl cyclohexane	...	2.10	—18.22	4.34	2436	1.825
3. Cyclohexanol ...	...	15.00	—62.04	14.86	2426	1.829
4. Methyl cyclohexanol	...	...	—61.28	14.69	2419	1.825
5. Cyclohexanyl acetate	...	...	—49.10	11.75	2429	1.826
6. Methyl cyclohexanyl acetate	...	...	—44.95	10.75	2431	1.829
7. Cyclohexanone ...	...	18.20	—66.07	15.79	2429	1.826
8. Methyl cyclohexanone	...	...	—61.97	14.88	2410	1.817

Rule<sup>11</sup> found that an increase in polarity of the solvent decreases the rotatory power, although for some optically active compounds the reverse occur.

According to Debye dipole association occurs between the polar molecules. When association of this kind occurs between a dipole in the optically active solute and another in the solvent, the field of force within the active molecules will be weakened and the contribution of the dipolar radical to the total optical activity of the molecule will be reduced. The more powerful the dipoles in the solvent, the greater will be the degree of dipole association between the solute and the solvent and the greater the observed change in optical rotation. With weakly polar solvents, solvation may lead to a tendency for the solvent dipoles to become loosely oriented towards the solute molecules giving rise to minor effects of the same kind.



Table 2

Temperature = 25°C

Solvent	Cyclohexane			Methyl cyclohexane			Cyclohexanol			Methyl Cyclohexanol		
Concentration grams/100 c.c.	2.4424			2.4420			2.4428			2.4420		
Calculated $\left\{ \begin{array}{l} [\alpha] \\ \lambda_0 \end{array} \right.$	$\frac{5.141}{-\lambda^2 - 0.05900}$ 0.2429			$\frac{4.346}{-\lambda^2 - 0.05934}$ 0.2436			$\frac{14.86}{-\lambda^2 - 0.05885}$ 0.2426			$\frac{14.69}{-\lambda^2 - 0.05850}$ 0.2419		
Line $\lambda$	Obs $[\alpha]$	Cal $[\alpha]$	Diff o-c	Obs $[\alpha]$	Cal $[\alpha]$	Diff o-c	Obs $[\alpha]$	Cal $[\alpha]$	Diff o-c	Obs $[\alpha]$	Cal $[\alpha]$	Diff o-c
Hg 4358	-39.30	-39.25	+0.05	-33.26	33.28	-0.02	-113.49	-113.40	+0.09	-111.89	-111.80	+0.09
Li 4603	33.64	33.66	-0.02	28.52	28.51	+0.01	97.24	97.20	+0.04	95.87	95.85	+0.02
Cd 4678	32.14	32.15	-0.01	27.26	27.23	+0.03	92.90	92.89	+0.01	91.66	91.60	+0.06
Cd 4800	30.03	30.00	+0.03	25.37	25.41	-0.04	86.62	86.66	-0.04	86.42	86.46	-0.04
Cd 5086	25.76	25.74	+0.02	21.84	21.79	+0.05	74.32	74.35	-0.03	74.22	74.23	-0.01
Cu 5106	25.53	25.49	+0.04	21.55	21.58	-0.03	73.66	73.64	+0.02	73.50	73.49	+0.01
Cu 5153	24.90	24.88	+0.02	21.08	21.07	+0.01	71.93	71.89	+0.04	71.72	71.75	-0.03
Cu 5219	24.11	24.09	+0.02	20.44	20.39	+0.05	69.62	69.60	+0.02	69.46	69.47	-0.01
Hg 5461	21.46	21.49	-0.03	18.22	18.19	+0.03	62.04	62.08	-0.04	61.28	61.29	-0.01
Cu 5700	19.35	19.33	+0.02	16.32	16.36	-0.04	55.82	55.85	-0.03	55.77	55.75	+0.02
Hg 5780	18.72	18.69	+0.03	15.80	15.81	-0.01	54.04	54.00	+0.04	53.96	53.92	+0.04
Na 5893	17.88	17.85	+0.03	15.06	15.09	-0.03	51.53	51.52	+0.01	51.48	51.45	+0.03
Li 6104	16.40	16.41	-0.01	13.90	13.87	+0.03	47.36	47.37	-0.01	47.36	47.31	+0.05
Cd 6438	14.50	14.47	+0.03	12.30	12.24	+0.06	41.80	41.79	+0.01	41.80	41.75	+0.05
Li 6708	13.11	13.15	-0.04	11.12	11.13	-0.01	37.94	37.99	-0.05	37.98	37.96	+0.02
	No mutarotation			No mutarotation			No mutarotation			No mutarotation		

Table 3

Temperature = 25°C.

Solvent		Cyclohexanyl acetate			Methyl cyclohexanyl acetate			Cyclohexanone			Methyl cyclohexanone		
Concentration grams/100 c.c.		2.4428			2.4416			2.4410			2.4408		
Calculated		$-\frac{11.75}{\lambda^2-0.05900}$ 0.2429			$-\frac{10.75}{\lambda^2-0.05910}$ 0.2431			$-\frac{15.79}{\lambda^2-0.05899}$ 0.2429			$-\frac{14.88}{\lambda^2-0.05808}$ 0.2410		
Line $\lambda$		Obs $[\alpha]$	Cal $[\alpha]$	Diff o-c	Obs $[\alpha]$	Cal $[\alpha]$	Diff o-c	Obs $[\alpha]$	Cal $[\alpha]$	Diff o-c	Obs $[\alpha]$	Cal $[\alpha]$	Diff o-c
Hg 4358		-89.66	-89.68	-0.02	-82.20	-82.16	+0.04	-120.67	-120.62	+0.05	-112.61	-112.70	-0.09
Li 4603		76.94	76.92	+0.02	70.42	70.40	+0.02	102.44	102.40	+0.04	96.84	96.84	+0.01
Cd 4678		73.45	73.47	-0.02	67.20	67.23	-0.03	98.80	98.78	+0.02	92.55	92.58	-0.03
Cd 4800		68.54	68.55	-0.01	62.75	62.76	-0.01	92.15	92.17	-0.02	86.44	86.40	+0.04
Cd 5086		58.86	58.82	+0.04	53.84	53.85	-0.01	79.12	79.09	+0.03	74.22	74.20	+0.02
Cu 5106		58.29	58.26	+0.03	53.10	53.07	+0.03	78.30	78.32	-0.02	73.30	73.28	+0.02
Cu 5153		56.88	56.86	+0.02	52.06	52.05	+0.01	76.44	76.46	-0.02	71.74	71.71	+0.03
Cu 5219		55.08	55.05	+0.03	50.42	50.40	+0.02	74.01	74.04	-0.03	69.42	69.45	-0.03
Hg 5461		43.10	49.11	-0.01	44.95	44.96	-0.01	66.07	66.05	+0.02	61.97	61.98	-0.01
Cu 5700		44.16	44.17	-0.01	40.40	40.43	-0.03	59.33	59.38	-0.05	55.76	55.75	+0.01
Hg 5780		42.70	42.71	-0.01	39.10	39.09	+0.01	57.46	57.43	+0.03	53.94	53.90	+0.04
Na 5893		40.79	40.75	+0.04	37.33	37.30	+0.03	54.86	54.80	+0.06	51.44	51.42	+0.02
Li 6104		37.41	37.47	-0.06	34.32	34.30	+0.02	50.40	50.38	+0.02	47.34	47.30	+0.04
Cd 6438		33.02	33.06	-0.04	30.28	30.25	+0.03	44.45	44.44	+0.01	41.70	41.73	-0.03
Li 6708		30.02	33.05	-0.03	27.55	27.50	+0.05	40.42	40.40	+0.02	37.90	37.93	-0.03
		No mutarotation			No mutarotation			No mutarotation			No mutarotation		

The sequence of decreasing rotatory power of abietic acid in cyclohexane and its derivatives are as follows : Cyclohexanone > Methyl cyclohexanone > Cyclohexanol > Methyl cyclohexanol > Cyclohexanylacetate > Methyl cyclohexanylacetate > Cyclohexane > Methyl cyclohexane.

The sequence of decreasing or increasing rotatory power does not run strictly parallel with that of the dielectric constants of the solvents. In spite of this some parallelism can be traced between the rotatory power of abietic acid and the dielectric constants of the solvents in which the rotatory power is determined.

The above mentioned sequence of decreasing rotatory power in different solvents are derived from the rotatory power data for  $\text{Hg}_{5461}$  (Table 1). The choice of this wavelength is purely arbitrary. The same sequence was found to hold good for abietic acid with other wavelengths. But this is not true for all optically active substances. It is, therefore, necessary for any strict comparison of rotatory power of a series of compounds that the effects of dispersion should be eliminated. This elimination is neither very easy nor very safe when the dispersion is complex, but when a linear relation is found to hold good as in this case, the extrapolation is both simple and accurate. In this case when the simple dispersion formula holds good, the effects of dispersion can be eliminated completely by using the rotation constant  $K$  of the one term equation of Drude as a measure of the absolute rotatory power of the medium. It refers to a wavelength  $\lambda$  where  $\lambda^2 - \lambda_0^2 = 1$  square micron and is not much greater than 10,000 A. U. The longest observed wavelength in these measurements  $\text{Li}_{6708}$  and an extrapolation from it to about 10,000 A.U. is easily permissible in view of the linear nature of the dispersion equations obtained from these measurements. Hence the values of  $K$ , the rotation constant as a measure of the absolute rotatory power of the substance are given in table 1. It would be found that the sequence of rotation constant  $K$  is the same as the optical rotation.

$\lambda_0^2$ , the dispersion constant in the Drude's equation represents the square of the wavelength of the dominant absorption band controlling the optical rotation.

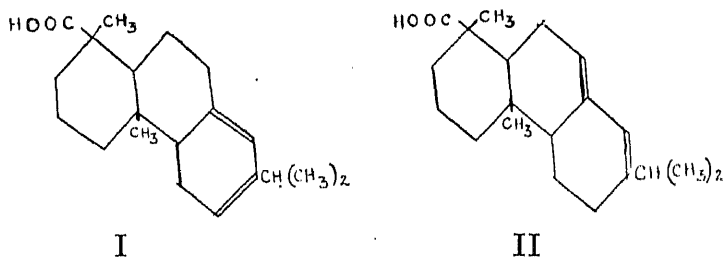
Pickard and Hunter<sup>12</sup> found that the rotatory dispersion of *d*- $\gamma$ -nonyl nitrite could be expressed by the equation

$$\alpha = \frac{0.76}{\lambda^2 - 0.135} + \frac{0.43}{\lambda^2}.$$

The dispersion constant  $\lambda_0^2 = 0.135$  corresponds with a characteristic wavelength  $\lambda_0 = 3680 \text{ \AA. U.}$  Direct measurements of absorption revealed a maximum at 3670 to 3720  $\text{\AA. U.}$  in good agreement with the wavelength deduced from measurements of rotatory dispersion. It, thus, appears that the characteristic absorption bands which rotatory dispersion equations predict have a real existence.

The characteristic absorption band  $\lambda_0$  for abietic acid in different solvents as obtained from measurements of rotatory dispersion are given in table 1.

The structure I was assigned to abietic acid from a study of the oxidation products but Ruzicka, Sternbach and Jeger<sup>13</sup> produced the most unequivocal chemical evidence for structure II which is now generally accepted.



Confirmatory evidence for structure II is supplied by Woodward's calculations<sup>14</sup> of the absorption spectra for normal conjugated dienes (the double bonds not lying in one ring).  $\lambda_{max}$  (calculated) for struc-

ture II is  $2420 \pm 5$  A. U. and  $\lambda_{max}$  for abietic acid observed by different workers by actual measurements of absorption are given below.

Kraft <sup>15</sup>	...	...	...	2375 A. U.
Harris & Sanderson <sup>16</sup>	...	...	...	2410 A. U.
Sanderman <sup>17</sup>	..	...	...	2400 A. U.

The values of absorption maxima obtained from rotatory dispersion measurements are found to be in very good agreement with the values obtained by actual measurement of absorption and with that calculated by Woodward's method.

The dispersion ratio is found to remain constant at 1.826.

It has been first observed by Dupont, Rouin and Dubourg<sup>18</sup> that the specific rotation of the rosin acids depend not only on the solvent used but also on the concentration in the solvent. Georgi<sup>19</sup> also observed the same phenomena. More systematic work on this point was undertaken in this laboratory and the result obtained for the rotation of abietic acid in different solvents are represented graphically in Figures II, III & IV. All the rotations measured are for  $Hg_{5461}$  at 25°C.

It is well known that most organic acids like benzoic acid are very strongly associated even in a dilute solution. It has been found that the electronegative group COOH confers the power of association to organic acids. Dupont, Rouin and Dubourg<sup>18</sup> have found from cryoscopic measurements that abietic acid is associated in alcohols. Moreover alcohols have been found to be the best associating solvent. They are themselves associated in solutions and when they act as solvents have the power of influencing the associating power of organic acids dissolved in them although this effect is least with alcohols as compared with other associating solvent. Moreover, combination between solute and solvent also take place which has the effect of reducing the

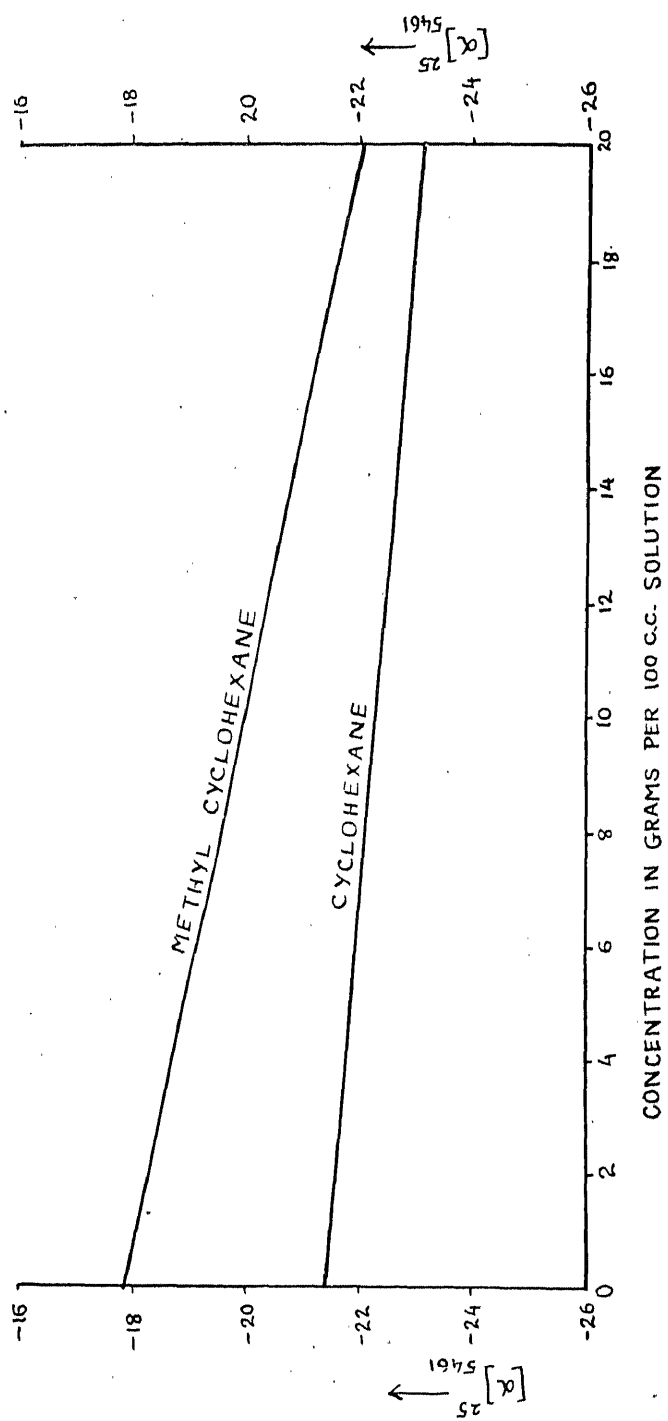


Fig.-II

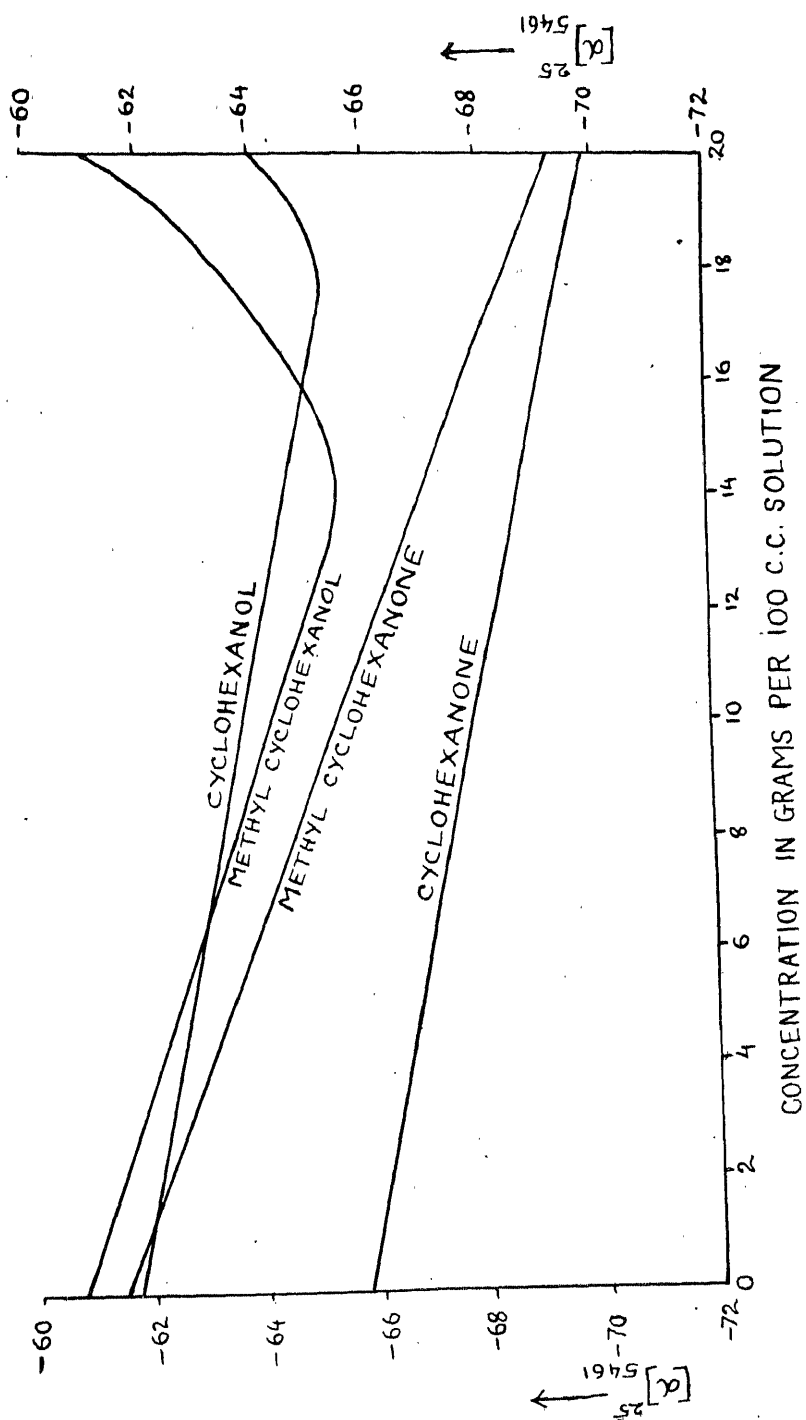


Fig.-III

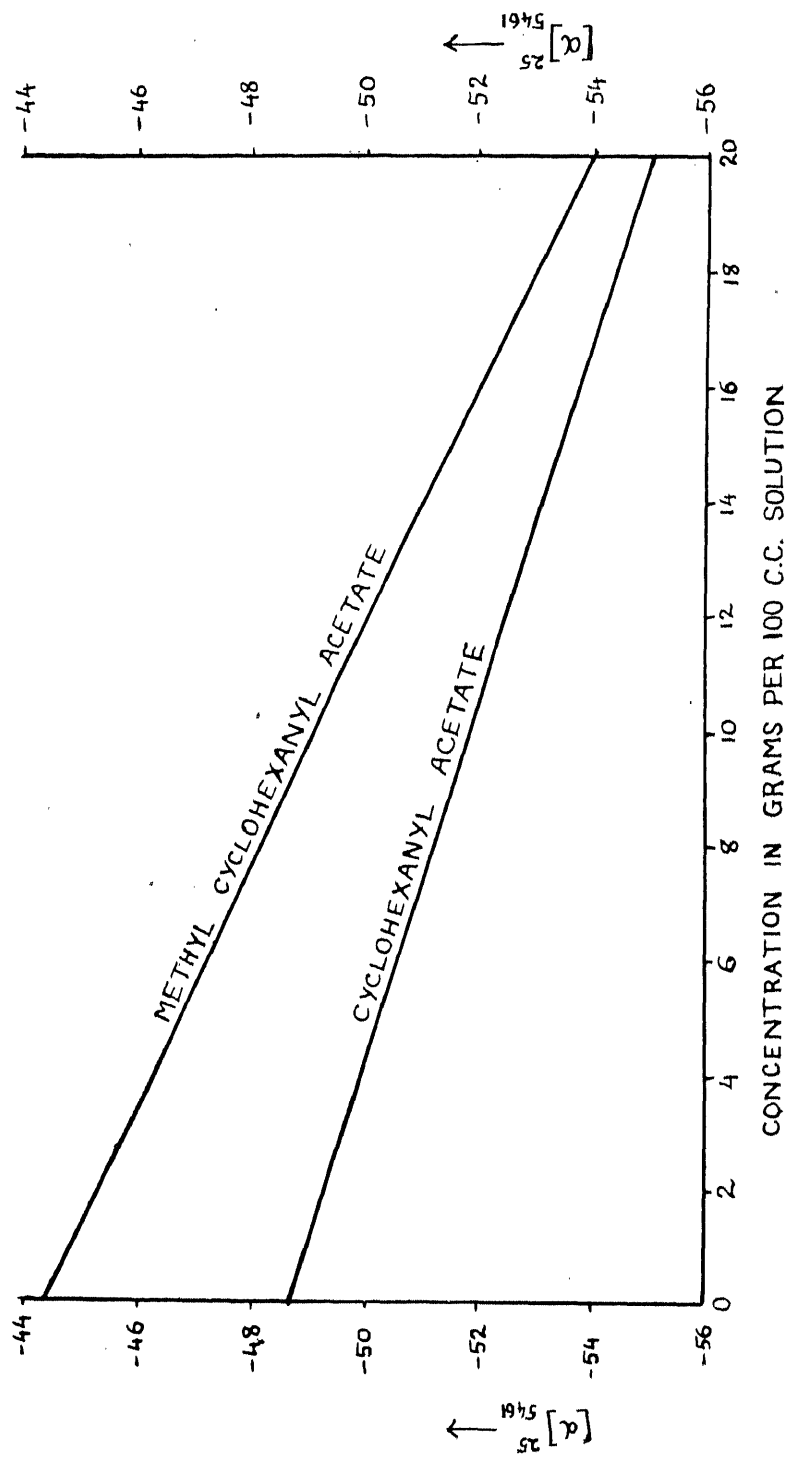


Fig.-V



amount of free solvent thereby concentrating the solution leading to a change in optical rotation. The results obtained for the optical rotation of abietic acid can easily be explained on the above basis of association and compound formation and subsequent dissociation of the complex molecules. With Cyclohexane, Methyl Cyclohexane Cyclohexanone Methyl cyclohexanone, Cyclohexanyl acetate, Methyl cyclohexanyl acetate there is a gradual increase of specific rotation with increasing concentration. But with cyclohexanol and Methyl cyclohexanol there is a gradual increase of specific rotation with increasing concentration up to a certain limit beyond which the specific rotation decreases. This point corresponds where the dissociation of complex molecules between solute and and solvent begins.

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